

AFOSR 4746

63-4-1

CATALOGED BY DDC  
AS AD No. 407611

AD

AF EOAR GRANT 62-34

TR

10 Nov. 1962

ANNUAL TECHNICAL REPORT

November 1961 - October 1962

NEW HYDRIDES OF TRANSITION METALS

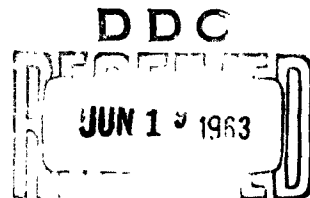
by

Prof. Lamberto Malatesta

Institute of General and Inorganic Chemistry

University of Milan (Italy)

The research reported in this document  
as been sponsored by, the  
OFFICE OF SCIENTIFIC RESEARCH, OAR  
through the European Office, Aerospace Research  
United States Air Force.



## ANNUAL TECHNICAL REPORT Nov. 1, 1961 - Oct. 31, 1962

INTRODUCTION REMARKS

The first part of this Report will describe the work so far carried out by M. Angoletta on iridium complex hydrides, which has been published in "Gazzetta Chimica Italiana" with the title "Trihydrido tris(triphenylphosphine)iridium compounds".

The second part of this note will shortly describe the work carried out by Freni and Valenti on rhenium complex hydrides. This work has given place to the discovery of two very interesting new compounds of this class, and will be ready for publication in about three months.

The research carried out on complex hydrides of gold by Malatesta and Naldini will be dealt with in part III. This research has led to the discovery of some very unusual derivatives of zerovalent gold. A research on complex hydrides of copper has been undertaken too, but only a few preliminary results will be given on this work, at present.

Finally the preliminary research on cobalt complex hydrides, undertaken by Malatesta and Sacco, has not given any important result and therefore was abandoned.

P A R T ITRIHYDRIDOTRIPHENYLPHOSPHINEIRIDIUM COMPOUNDS

by L. Malatesta and M. Angoletta

A few years ago Chatt(1) observed that the trialkylphosphine derivatives of some metals, belonging to the group VIII of Mendeleieff table, can easily be transformed in hydridohalogenotrialkylphosphine metals and in hydridotrialkylphosphine metals. Platinum (1), osmium and ruthenium (2) appear to give the most stable compounds, nickel(3) and palladium (4) the least stable.

All these compounds have formulas  $MHXL_4$  or  $MH_2L_4$  ( $X = Cl; Br; I; L = \text{trialkylphosphine}$ ) and are stable to air. They have well defined composition with a probably octahedral structure; the monohydrides are considered to have the hydrogen atoms trans to the halogen and the dihydrides the hydrogen atoms trans each other. These compounds show a very intense absorption band in the I.R., at about  $2000\text{ cm}^{-1}$ , due to the metal-hydrogen stretching; this band shifts to about  $1400\text{ cm}^{-1}$  on deuteration. The N.M.R. absorption (1,2) gives further evidence for the presence of the hydrido atoms.

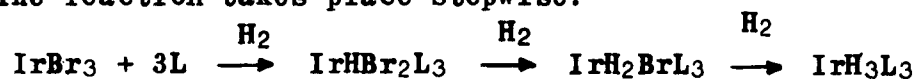
Among the metals of the cobalt group (Co, Rh, Ir) only iridium seems to give stable hydrides: preliminary notes on compounds of this type with triphenylphosphine were made by Malatesta and coworkers, by Hayter (5) and by Vaska (6), while Chatt (7) reported the hydrido complex with triethylphosphine.

We found now, for the first time, and we succeeded in separating, the two isomeric forms of trihydridotris(triphenylphosphine)iridium.

ridium, and we studied the very interesting reaction of these isomers with perchloric acid, as we will describe in the following pages.

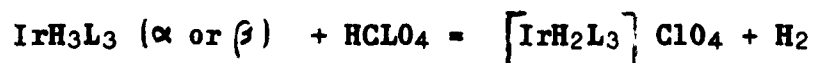
The transformation of the halogenotriphenylphosphine compounds in the corresponding trihydrides is best carried out using sodium tetrahydridoborate as reducing agent in ethanolic solution or, more exactly, treating with this reagent the suspension obtained by mixing an ethanolic solution of  $\text{IrBr}_3(\text{H}_2\text{O})_x$  with an ethanolic solution of the phosphine:  $\text{P}(\text{C}_6\text{H}_5)_3 = \text{L}$ .

The reaction takes place stepwise:



and, with a defect of reducing agent, the dihydridomonobromocompound can easily be isolated. With an excess of sodium tetrahydridoborate a white crystalline precipitate is readily obtained. This can be separated by fractional crystallisation in two different compounds, which from analysis and properties have been recognized as the two isomers of  $\text{IrH}_3\text{L}_3$ .

The number of hydrogen atoms in these compounds cannot be determined directly by analysis, neither was a reaction found which gave place to the quantitative evolution of all this hydrogen. We have however reached indirect evidence for the presence of the three hydrido atoms. In fact the two hydrides, indicated as  $\alpha$  (high melting form) and  $\beta$  (low melting form) resp., react with dilute perchloric acid in ethanol giving exactly 1 mol<sup>cf</sup> hydrogen and forming the same perchlorate:



The perchlorate by reaction with NaBr gives by exchange the corresponding bromide in which the presence of two hydrido hydrogens has been

4-

proved.<sup>(6)</sup> This compound shows two absorption bands at  $2222\text{ cm}^{-1}$  and  $2128\text{ cm}^{-1}$ , which are expected for two hydrogen atoms in non-equivalent positions.

The fact that the two isomers give the same perchlorate is easily explained if we admit that the insaturated cation  $[\text{IrH}_2\text{L}_3]^+$  readily rearranges to give the most stable form.

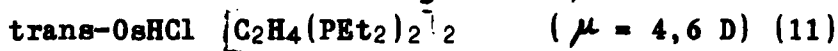
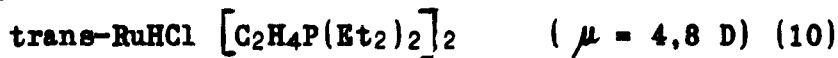
The perchlorate  $[\text{IrH}_2\text{L}_3][\text{ClO}_4]$  is a very insaturated compound ; in benzenic solution it behaves as an ionic couple with a moment of 13,4 Debye units and in acetone solution as a uni-uni-valent electrolyte. It easily co-ordinates every kind of ligands ( $\text{NH}_3$ , pyridine, triphenylphosphine, halides ions;  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , etc.), reassuming its coordinative saturation.

The trihydridotristriphenylphosphine compounds, with the only exception of some rhenium hydrides (8) of a quite different type, represent the first case where three hydrogen atoms, bound to the same transition metal, have been observed, and the first case of isomeric hydrides. In fact all the hydrido derivatives of Fe(9), Ru(2), Os(2) and Ir(7), described by Chatt, have been obtained only in one form, neither did Hayter observe, in his preliminary note, that the trihydridotris(triphenylphosphine)iridium is obtained as a mixture of two isomers.

Evidence for the structure of these isomeric forms has been obtained from their electric moments and from their I.R. spectra. The measurements made by Chatt (10,11,12) of the electric moment of some hydridophosphine coordination compounds and of some halogeno-carbonylmetals allowed us to make some rough estimation on the electric moment to be expected for the two isomers, and to compare these estimations with the experimental figures. Chatt gives  $\mu = 4,65$  for the planar compound  $\text{PtCl}_2(\text{CO})_2$  (10) and estimates the Pt-CO bond moment about 0,5 D (Positive end of the moment on CO). From these figures

$\text{Pt-Cl} = (4,65/\sqrt{2}) - 0,5 = 2,8 \text{ D}$  is obtained.

If now we admit that in this type of compounds the metals Ru, Os, Ir and Pt have about the same chlorine-metal moments, from the following figures:



we find for the bond moment  $\text{M-H}$  a value of  $\mu = 1,4 - 2,0 \text{ D}$ , with the positive end on the hydrogen atom.

The difference between the  $\text{M} \rightarrow \text{P}(\text{C}_6\text{H}_5)_3$  moment, which Chatt estimates as  $3,3 - 3,4 \text{ D}$  (positive end on the phosphine) and the just calculated bond moment  $\text{M-H} = 1,4 \sim 2,0$ , that is  $(4,3 \sim 4,4) - (1,4 \sim 2) = 2,3 \sim 3 \text{ D}$ , should give the moment  $\text{H-Me-P(Ph)}_3$  when the ligands are at  $180^\circ$ . This is also the moment to be expected for the trans form of  $\text{IrH}_3\text{P}_3$ , if there is no distortion of the octahedron.

The experimental determination for the  $\alpha$  - form gave  $\mu = 2,3 \text{ D}$ .

The so called  $\alpha$  - form is therefore to be considered the trans form.

The cis isomer, if there are no distortions, should have a moment 1,73 times larger. The bulkiness of the three triphenylphosphine molecules on the same face of the octahedron are likely to give some distortion, so that the calculated figure  $\mu = 3,9 \sim 5,1 \text{ D}$  should be considered a maximum. The value  $\mu = 3,5 \text{ D}$  can be therefore considered in satisfactory agreement with the value calculated for the cis form.

The evidence of the I.R. spectrum seems to confirm, though not in a rigorous way, the results of the electric moments.

From symmetry considerations two bands should be expected for the (undistorted) cis compound and three for the trans compound, instead of one (at  $2080 \text{ cm}^{-1}$ ) and two (at  $1730$  and  $2100 \text{ cm}^{-1}$ )

respectively. No conclusion can therefore be derived from the number of these bands. On the other hand we observed that the hexacoordinated hydridophosphine compounds show an absorption at about  $1750\text{ cm}^{-1}$  only when two hydrogen atoms are trans each/other. Now the compound which, from the electric moment, is to be considered the trans-trihydridotristriphenylphoshineiridium shows a band in this region and we consider this should be taken as an additional evidence for the assigned structure.

#### R e f e r e n c e s

- 1) J. Chatt, L.A. Duncanson and B.L. Shaw, Proc.Chem.Soc., 1957, 343
- 2) J. Chatt and R.G. Hayter, J. Chem. Soc., 1961, 2605
- 3) M.L.H. Green, H. Street and G. Wilkinson, Z. Naturforsh., 14 B. 738 (1959)
- 4) J. Chatt. L.A. Duncanson and L.B. Shaw, Chem. and Ind., 1958, 859; Proc. Chem. Soc., 1957, 343
- 5) R.G. Hayter, J. Am. Chem. Soc., 83, 1259 (1961)
- 6) L. Vaska, J. Am. Chem. Soc., 83, 756 (1961)
- 7) J. Chatt, Proc. Chem.Soc., 1962, 321
- 8) A.P. Ginsberg, J.M. Miller and E. Koubet, J. Am. Chem. Soc., 85, 4909 (1961)
- 9) J. Chatt and R.G. Hayter, J. Chem. Soc., 1961, 6607
- 10) J. Chatt and A.A. Williams, J. Chem. Soc., 1951, 3061
- 11) J. Chatt and Hayter, J. Chem. Soc., 1961, 2605
- 12) J. Chatt and F.A. Hart, J. Chem. Soc., 1961, 1378

## P A R T E I I

### NEW RHENIUM TRIPHENYLPHOSPHINE HYDRIDES

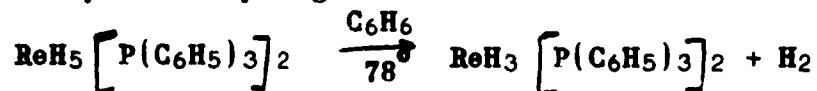
by

M. Freni and V. Valenti

The researches carried out in these laboratories before the assignment of the Grant 62/34, led to the preparation of two rhenium phosphine hydrides, (1) namely  $\text{ReH}_3 [\text{P}(\text{C}_6\text{H}_5)_3]_2$  and  $\text{ReH}_3 [\text{P}(\text{C}_6\text{H}_5)_3]_4$ .

During subsequent work, carried out on these compounds under Grant 62/34, two new complex rhenium hydrides, with triphenylphosphine as ligand, have been obtained.

In fact from the reaction liquor of  $\text{ReOX}_2(\text{OC}_2\text{H}_5)[\text{P}(\text{C}_6\text{H}_5)_3]_2$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) with  $\text{NaBH}_4$ , from which the red  $\text{H}_3\text{Re} [\text{P}(\text{C}_6\text{H}_5)_3]_2$  had previously been obtained, a new more soluble, white compound was isolated; to this compound the formula  $\text{ReH}_5 [\text{P}(\text{C}_6\text{H}_5)_3]_2$  was provisionally assigned. This compound is diamagnetic and non conductor; on boiling its benzenic solution it forms the red compound containing three hydridic hydrogen atoms



Its I.R. spectrum shows a broad band at  $1875 \text{ cm}^{-1}$ , which however is much less intense and less resolved than the metalhydrogen stretching bands of other hydrides, for instance of the iridium phosphine hydrides (2).

The N.M.R. spectrum shows clearly the presence of hydridic hydrogen, but the compound is not soluble enough to give a spectrum which could be interpreted quantitatively.

The only way by which we could determine the number of these hydrogen atoms was by evolution with iodine in xylene.

We consider that the evidence obtained indicates that



five hydrogen atoms are the most probable figure.

Another compound, whose analysis with iodine in xylene indicates as having a number of hydridic hydrogen atoms intermediate between  $\text{ReH}_3 [\text{P}(\text{C}_6\text{H}_5)_3]_2$  and the supposed  $\text{ReH}_5 [\text{P}(\text{C}_6\text{H}_5)_3]_2$ , was isolated <sup>by</sup> treating the compound  $\text{ReH}_3 [\text{P}(\text{C}_6\text{H}_5)_3]_4$  with  $\text{NaBH}_4$  in benzene suspension. This compound, to which we attribute the formula  $\text{ReH}_4 [\text{P}(\text{C}_6\text{H}_5)_3]_3$  is very soluble and can be recovered from the benzene solution by precipitation with ethanol. It is yellow, diamagnetic, very stable, and shows two not very intense H-stretching bands at 1900, 1970  $\text{cm}^{-1}$ .

The determination of the N.M.R. spectrum is in course.

#### R e f e r e n c e s

- 1) M. Freni and V. Valenti, Gazzetta Chim. It., 91, 1357 (1961)
- 2) M. Angoletta, Gazzetta Chim. It. 92, 811 (1962).

# P A R T E   I I I

## COMPLEX HYDRIDES OF COPPER, SILVER AND GOLD

by            L. Malatesta and L. Naldini

In the reaction of  $\text{AuCl} \cdot [\text{P}(\text{C}_6\text{H}_5)_3]$  with  $\text{NaBH}_4$  we obtained a compound whose formula is :  $\text{Au} \cdot \text{P}(\text{C}_6\text{H}_5)_3$ ; also deriving from monovalent gold. This product seems to change its molecular complexity with time; the molecular weight of the least polymerized fraction (most soluble fraction) was between 3 and 4 times that of the monomer.

Silver seem~~s~~ to give analogous compounds but we have not yet isolated them.

With copper we obtained on the contrary a hydride, corresponding to  $[(\text{C}_6\text{H}_5)_3\text{P}]_2 \text{CuH}_4\text{B}$ , which has a very interesting I.R. spectrum, with two orders of bands at  $2400 \text{ cm}^{-1}$  and at  $2000 \text{ cm}^{-1}$  r~~es~~sp.

We are carrying out this work very actively at present and we hope to have some result~~s~~ for publication in the next months.